Abstract No. chan202

Synchrotron X-Ray Radiolysis Mechanisms of Amino Acid Modification of Proteins

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Beamline(s): X28C

In order to elucidate reaction mechanisms for side chain modifications of amino acids in peptides and proteins, radiolysis experiments in ^{18}O-labeled water were carried out at X9-A beamline. Mass spectrometry techniques are being applied to characterize the reaction products. Radiolysis of peptides in ^{18}O-labeled water under aerobic conditions revealed that oxygenated radical species from air and water both contribute to the modification of amino acid side chains. Cysteine and methionine side chains reacted with hydroxyl radicals generated from radiolysis of water as well as molecular oxygen. Phenylalanine and tyrosine residues were modified predominantly by hydroxyl radicals, and the source of modification of proline was exclusively through molecular oxygen.

These studies are being extended to other amino acid residues. Additionally, ^{18}O-labeled oxygen will be used to further explain the role of oxygen and the mechanism of oxidation of amino acids in synchrotron X-ray radiolysis protein footprinting experiments.